Vanadium

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V

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Element Data
*Atomic Symbol: **V***
*Atomic Number: **23***
Atomic Weight: 50.9415 g/mol
Isotopes and Abundances: ^{50}V *0.25 %*, ^{51}V *99.75 %*
1 Atm Melting Point: 1910 °C
1 Atm Boiling Point: 3407 °C
Common Valences: 5+, 4+, 3+, 2+
Ionic Radii: 64 pm (in 3+, 6-fold coordination)
Pauling Electronegativity: 1.63
First Ionization Energy: 6.74 eV
Chondritic (CI) Abundance: 54.6 ppm[a]
Silicate Earth Abundance: 86 ppm[a]
Crustal Abundance: 138 ppm[b]
Seawater Abundance: ~30–37 nmol/kg[c]
Core Abundance: ~150 ppm[d]
[a]*Palme et al. (2014)*
[b]*Rudnick and Gao (2014)*
[c]*Bruland et al. (2014)*
[d]*McDonough (2014)*

Properties

Vanadium (chemical symbol, V) is a d-block transition metal, silver in color, appearing in the first long period of the periodic table between titanium and chromium. Vanadium has two stable isotopes: ^{50}V and ^{51}V, with atomic abundance of 0.25 % and 99.75 %, respectively. Vanadium has several oxidation forms (between 2+ and 5+). In the lithosphere, V occurs as reducing V(III) form, whereas in oxidizing conditions V prevails under V(IV) form. Vanadium(II) is particularly unstable in the environment. Vanadium(III) is more stable than V(II), but it is also gradually oxidized by the air or dissolved oxygen. Vanadium(V) is expected to be the prevailing form in waters exposed to atmospheric oxygen, whereas V(IV) may be present in reducing environments. Depending upon geometry and environment, V ionic radii vary between 36 pm and 79 pm. Vanadium has a high melting point of 1910 °C and is a mildly incompatible, refractory, lithophile (siderophile in the iron core and chondrites) element. Vanadium has an electronegativity of 1.63 on the Pauling scale and displays a first ionization potential of 6.74 eV. More details can be found in Richards (2006) and Haynes (2015).

History and Use

Vanadium was first discovered by del Rio in 1801 and was incorrectly considered as impure chromium. Vanadium was rediscovered and named by Sefström in 1830 after the Scandinavian goddess Vanadis. In 1867, Roscoe isolated V in nearly pure form by reducing V chloride with hydrogen. Vanadium of high purity (99.3–99.8 %) was not produced until 1927. The V redox chemistry and its specific application to renewable energy technologies (e.g., vanadium redox battery; a type of rechargeable flow battery using V in different oxidation states to store chemical potential energy) have already add to the demand for this element and will definitely continue to increase in the near future. Vanadium demand for construction materials is the greatest consumer of mined V - (Moskalyk and Alfantazi, 2003). Indeed, vanadium is the most widely used alloying element for strengthening steels employed in buildings and bridges. Vanadium volume that is cycled through terrestrial and aquatic reservoirs can thus be

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expected to further growth. It results in uncontrolled V releases in the environment, and environmental issues appear in developing and developed countries (Imtiaz et al., 2015).

Geochemical Behavior

Widely and sparsely distributed, V is not found as the free metal in nature. It originates from primary sources such as ores (i.e., iron oxides deposits), metallurgical slags (i.e., processing of U and Ti ores), and petroleum residues. Other sources include vanadiferous sandstones, bauxite, coals, or oil shales.

Vanadium is widely distributed in igneous and sedimentary rocks and minerals. Among more than fifty minerals, carnotite [$K_2(UO_2)_2(VO_4)_2.3H_2O$], roscoelite [$KV^{3+}{}_2(Si_3Al)O_{10}(OH)_2$], vanadinite [$Pb_5(VO_4)_3Cl$], mottramite [$PbCu(VO_4)(OH)$], and patrónite ($VS_4$) are the most important V-carriers. It is also present in some crude oils as organic complexes. Its average content in the Earth's crust is approximately 138 ppm and is similar to that of Zn and Ni. It is, however, more dispersed in the crust than either of those elements, and concentrated mineral deposits are consequently rare. The average V contents of CI chondrites range from 54.6 ppm to 56.5 ppm. The silicate Earth has a V content of 86 ppm, the bulk Earth of 105 ppm, whereas its content in the metallic core is slightly higher (150 ppm). Vanadium contents in the bulk continental crust vary significantly from 96 ppm to 230 ppm. These aspects have been further reviewed by McDonough (2014), Palme et al. (2014), and Rudnick and Gao (2014).

Historically, geochemists' interest in vanadium has derived from the occurrence of variable redox states in Earth surface environments, +3, +4, +5, and as a consequence its application as a redox indicator (Huang et al., 2015). Indeed, V chemical speciation and solubility are strong functions of pH and Eh conditions. Incorporation of reduced V species (III, IV) in clays and other secondary minerals provides a useful redox indicator for past anoxic conditions. Moreover, V behaves as an incompatible element because V(III) is preferentially incorporated into crystals: V-bearing minerals which crystallized in equilibrium with a low fO_2 magma have a higher V content than crystals from the same magma with high fO_2 (Mallmann and O'Neill, 2009). It results in an increasing interest in V partitioning during high temperature – high pressure magma differentiation processes. Studies on V partitioning among Earth's crustal reservoirs have provided critical insights into the interaction and evolution of these reservoirs. Vanadium depletion in the silicate Earth is explained by it preferential partitioning into the metallic core during "deep magma ocean" process (at high pressure and low fO_2; Wood et al., 2006). The core could contain half of the total V budget of the bulk Earth (McDonough, 2014). Perspectives to exploit V stable isotope chemistry are considered: Wu et al. (2015) proposed first-principles calculations that predict V isotopes fractionation among V species with different valences in aqueous systems and during sorption of V(V) to goethite.

Vanadium is also a naturally occurring element in air, soil, plants, and water. The concentration of dissolved V in natural freshwater and seawater is generally several mg/L or lower (Bruland et al., 2014; Gaillardet et al., 2014). Vanadium concentrations in marine and nonmarine sediments are generally below 100 ppm, reflecting a net accumulation from the aqueous phase. Vanadium in trace amounts represents an essential element for normal cell growth, but it may cause adverse effects when its concentration is much greater than a few tenths of μg/L (Chatterjee, 2009). Most data on the release of V into the environment have been related to industrial activities, especially from oil refineries and power plants using V-rich fuel oil, and coal crude oil is enriched in V with respect to many other trace elements, with concentrations occasionally exceeding 1 mg/L. Thus, the fraction of dissolved V in surface waters might be an environmental indicator of oil combustion or pollution (Hope, 2008). Such pollution sources may be responsible for appreciable amounts of V into the environment, well above the natural background levels associated with rock weathering and sediment leaching. Fluvial dissolved V concentrations might also be indicative of the types of rocks being weathered or of the nature of the involved weathering processes. Weathering rate and source rock type, rather than solution chemistry or anthropogenic influences, appeared to be the important controlling factors on fluvial dissolved V concentrations (Hope, 2008).

The oxidation rate of V(IV) to V(V) and the equilibrium between these two species in aqueous solution will regulate V prevalence in water (Pourret et al., 2012). It further depends on several factors, such as pH, V concentration, redox potential, ionic strength of the aqueous system, and biological activity. In water, V(IV) is commonly present as a vanadyl cation [VO^{2+}, $VO(OH)^{+}$], whereas V(V) exists as a vanadate oxyanion ($H_2VO_4^-$, HVO_4^{2-}). VO^{2+} is strongly adsorbed onto solid phases, including organic and oxyhydroxide phases. Adsorption of anionic V ($H_2VO_4^-$, HVO_4^{2-}) is much lower than the cations; however, VO^{2+} solubility may be greatly increased through complexation with organic matter. Whereas V(IV) is not thermodynamically stable at pH $>$ 7, complexation by various organic and inorganic species may considerably increase its stability. Eventually, V (V) oxidation state ion is more toxic than V(IV) ion one.

Biological Utilization and Toxicity

Whereas low concentrations of V are required for plants to positively influence chlorophyll synthesis, K consumption, or N assimilation, higher V concentrations are toxic as they cause chlorosis and limit growth. At trace amounts V is essential for normal cell growth, whereas possibly toxic at high concentrations, especially when occurring as pentoxide. Chronic exposure may result in inflammation of bronchi and trachea, eyes and skin irritation, pulmonary edema, and systemic poisoning.

Summary

Vanadium's occurrence receives more attention as the global demand for V increases. However, its prevalence in environment becomes a new critical issue. Vanadium has been suggested to be a potentially dangerous pollutant, and the United States Environmental Protection Agency classifies V in the priority list of environmental risk elements. Fixing the environmental issue of V is constrained by the limited understanding of V biogeochemistry relative to other d-block transition metals. A better understanding of V biogeochemical behavior may support to assess the risk to the environment and to human health and to assist in developing new remediation tools.

Cross-References

- ▶ Complexation
- ▶ Lithophile Elements
- ▶ Oxidation-Reduction
- ▶ Transition Elements

References

Bruland, K. W., Middag, R., and Lohan, M. C., 2014. 8.2 – controls of trace metals in seawater. In Holland, H. D., and Turekian, K. K. (eds.), *Treatise on Geochemistry*, 2nd edn. Oxford: Elsevier, pp. 19–51.

Chatterjee, M., 2009. Vanadium. In Schwab, M. (ed.), *Encyclopedia of Cancer*. Berlin/Heidelberg: Springer, pp. 3140–3142.

Gaillardet, J., Viers, J., and Dupré, B., 2014. 7.7 – trace elements in river waters. In Holland, H. D., and Turekian, K. K. (eds.), *Treatise on Geochemistry*, 2nd edn. Oxford: Elsevier, pp. 195–235.

Haynes, W. M., 2015. *CRC Handbook of Chemistry and Physics*, 96th edn. Boca Raton: CRC Press.

Hope, B. K., 2008. A dynamic model for the global cycling of anthropogenic vanadium. *Global Biogeochemical Cycles*, **22**, GB4021.

Huang, J.-H., Huang, F., Evans, L., and Glasauer, S., 2015. Vanadium: global (bio)geochemistry. *Chemical Geology*, **417**, 68–89.

Imtiaz, M., Rizwan, M. S., Xiong, S., Li, H., Ashraf, M., Shahzad, S. M., Shahzad, M., Rizwan, M., and Tu, S., 2015. Vanadium, recent advancements and research prospects: a review. *Environmental International*, **80**, 79–88.

Mallmann, G., and O'Neill, H. S. C., 2009. The crystal/melt partitioning of V during mantle melting as a function of oxygen fugacity compared with some other elements (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr and Nb). *Journal of Petrology*, **50**, 1765–1794.

McDonough, W. F., 2014. 3.16 – compositional model for the Earth's core. In Holland, H. D., and Turekian, K. K. (eds.), *Treatise on Geochemistry*, 2nd edn. Oxford: Elsevier, pp. 559–577.

Moskalyk, R. R., and Alfantazi, A. M., 2003. Processing of vanadium: a review. *Minerals Engineering*, **16**, 793–805.

Mukherjee, B., Patra, B., Mahapatra, S., Banerjee, P., Tiwari, A., and Chatterjee, M., 2004. Vanadium – an element of atypical biological significance. *Toxicology Letters*, **150**, 135–143.

Palme, H., Lodders, K., and Jones, A., 2014. 2.2 – solar system abundances of the elements. In Holland, H. D., and Turekian, K. K. (eds.), *Treatise on Geochemistry*, 2nd edn. Oxford: Elsevier, pp. 15–36.

Pourret, O., Dia, A., Gruau, G., Davranche, M., and Bouhnik-Le, C. M., 2012. Assessment of vanadium distribution in shallow groundwaters. *Chemical Geology*, **294**, 89–102.

Rehder, D., 2008. *Bioinorganic Vanadium Chemistry*. [illegible]y, 213 pp.

Richards, R. L., 2006. Vanadium: inorga[illegible] coordination chemistry. In *Encyclopedia of Inorganic Chemistr[illegible]*ley.

Rudnick, R. L., and Gao, S., 2014. 4.1 – composition of the continental crust. In Turekian, H. D., and Holland, K. K. (eds.), *Treatise on Geochemistry*, 2nd edn. Oxford: Elsevier, pp. 1–51.

Wood, B. J., Walter, M. J., and Wade, J., 2006. Accretion of the Earth and segregation of its core. *Nature*, **441**, 825–833.

Wu, F., Qin, T., Li, X., Liu, Y., Huang, J.-H., Wu, Z., and Huang, F., 2015. First-principles investigation of vanadium isotope fractionation in solution and during adsorption. *Earth and Planetary Science Letters*, **426**, 216–224.